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NASA TN D-5521

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EFFECTS OF BIAS LIGHT
AND HEAT TREATMENT ON THE
SPECTRAL RESPONSE OF CADMIUM
SULFIDE THIN FILM PHOTOVOLTAIC CELLS

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0132115

1. Report No. NASA TN D-5521		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle EFFECTS OF BIAS LIGHT AND HEAT TREATMENT ON THE SPECTRAL RESPONSE OF CAD- MIUM SULFIDE THIN FILM PHOTOVOLTAIC CELLS				5. Report Date January 1970	
7. Author(s) Henry W. Brandhorst, Jr., Rose L. Schalla, Andrew E. Potter, Jr., and Louis Rosenblum				6. Performing Organization Code	
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135				8. Performing Organization Report No. E-5193	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546				10. Work Unit No. 120-33	
15. Supplementary Notes				11. Contract or Grant No.	
16. Abstract Red and blue bias lights and heat treatment have complex effects on the spectral response of cadmium sulfide solar cells. These effects have been studied and are interpreted in terms of a model involving a photoconductive layer with a high dark resistance. In darkness or in red (0.9 μ m) light, this layer causes losses in the externally observed current both by its resistance and by trapping and recombination processes. Blue light (0.5 μ m) eliminates these losses. This layer is presumably formed in the junction region of the cell by diffusion of copper into the cadmium sulfide during heat treatment.				13. Type of Report and Period Covered Technical Note	
17. Key Words (Suggested by Author(s)) Cadmium sulfide Spectral response Heat treatment Solar cell				14. Sponsoring Agency Code	
18. Distribution Statement Unclassified - unlimited					
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 20	
				22. Price * \$3.00	

*For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151

EFFECTS OF BIAS LIGHT AND HEAT TREATMENT ON THE SPECTRAL RESPONSE OF CADMIUM SULFIDE THIN FILM PHOTOVOLTAIC CELLS

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SUMMARY

Cadmium sulfide (CdS) solar cells consist of an evaporated layer of n-type CdS covered with a thin film of p-type cuprous sulfide (Cu_2S). After a heat treatment, which is required for good junction characteristics, the spectral response of this cell is complex. For measurements made with only a monochromatic light beam ranging in wavelength from 0.375 to 1.2 micrometers, the past history of illumination of the cell influences the response. Furthermore, the response in the red end of the spectrum (0.7 to 1.2 μm) is almost nonexistent. When red bias light (0.9 μm) illuminates the cell in addition to the primary monochromatic light, a response similar to that obtained in the absence of bias light is obtained. The major difference is that the relative quantum yield measured in the visible region is very much greater than with no bias light. When blue bias light (0.5 μm) illuminates the cell, the response is much broader, extending from 1.0 to 0.375 micrometer (1.2 to 3.3 eV; 1.92 to 5.28×10^{-19} J). Changes in the intensity of bias and primary monochromatic light also change the response.

The effects of heat treatment at 220°C for up to $16\frac{1}{2}$ minutes were studied. The response in the red end of the spectrum, measured with no bias light, was diminished after several minutes of heating. Blue bias light eliminated the loss; however, the overall response had dropped nearly a factor of 2 during the treatment.

The effects of both bias illumination and heat treatment have been interpreted in terms of a model involving a photoconductive layer that has a high dark resistance. Blue light lowers the resistance of this layer. It is suggested that this layer is formed in the junction region of the cell by diffusion of copper into the CdS during heat treatment.

The high quantum yields observed with red bias light were determined to be spurious because the measurement technique did not account for the high losses due to the photoconductive layer when illuminated by red light alone.

INTRODUCTION

Present day cadmium sulfide thin film solar cells convert sunlight into electricity with an efficiency between 3 and 4 percent (air mass zero; 25⁰ C). This efficiency when coupled with their light weight and flexibility makes this type of solar cell attractive for use in space. These cells consist of an evaporated layer of cadmium sulfide covered with a semitransparent film of copper sulfide formed by the chemical displacement of cadmium by copper (refs. 1 and 2). In order to increase the efficiency of the cadmium sulfide cell, it is necessary to understand the mechanism of the photovoltaic effect in this device. Spectral response measurements are an important tool in contributing to the understanding of photovoltaic processes in general. Hence it was reasonable to measure the response of the CdS cell to further understand the photovoltaic mechanism in that device.

The spectral response of the cell is unusual in two respects. First, much of the response is extrinsic to cadmium sulfide, occurring in the 1.2- to 2.4-eV (1.92- to 3.84×10^{-19} -J) range. This response is thought to originate from the copper sulfide layer (refs. 3 and 4). Second, the spectral response is changed by illumination with secondary or bias light. Both red and blue bias lights affect the spectral response. For example, steady illumination of the cell with blue light greatly increases cell response to red and infrared light. This effect is not found until after heat treatment and has been explained as due to a blue-sensitive photoconductive layer formed by diffusion of copper into the cadmium sulfide (refs. 3 and 4).

The purpose of the research reported here was to make a detailed study of the effect of bias light on the spectral response of CdS thin film solar cells. This work is an extension of that previously reported by Potter et al. (ref. 5). Experiments were done with both red and blue bias light. Relative quantum yields were measured for primary monochromatic illumination from 1.2 to 3.3 eV (1.92 to 5.28×10^{-19} J) with red, blue, and no bias light. The effects of light intensity and heat-treatment time on the relative quantum yield were also studied.

DESCRIPTION OF EXPERIMENT

Construction of the Cell

A sketch of the cross section of a cadmium sulfide thin film cell is shown in figure 1. It consists of a layer of n-type cadmium sulfide (CdS) 20 to 40 micrometers thick on a metal foil or metallized plastic substrate 25 to 50 micrometers thick and a p-type copper sulfide (Cu₂S) barrier layer 0.1 to 0.3 micrometer thick, which is formed on the entire upper surface of the CdS film. A fine copper- or gold-mesh collector grid is

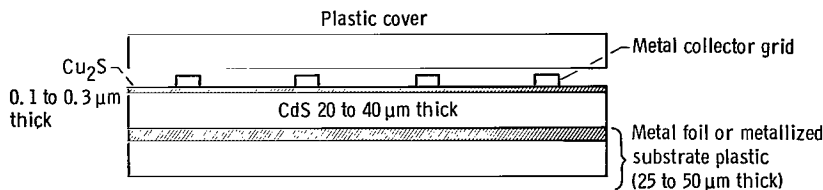


Figure 1. - Cross section of a CdS thin film solar cell.

pressed to the Cu_2S layer. Leads are attached to the metal foil substrate and to the collector grid, and a transparent plastic film cover is applied with a 225°C lamination process.

The cadmium sulfide layer is prepared by vacuum evaporation. The copper sulfide layer is formed by etching the cadmium sulfide film briefly in acid and then dipping it in a saturated aqueous solution of cuprous chloride for 5 seconds at 90°C (ref. 1). The layer consists of chalcocite, Cu_2S , grown epitaxially on the CdS surface by chemical displacement (ref. 2).

After the barrier layer is formed by the dipping process, the cells are washed in deionized water and dried in argon. At this stage, the cell efficiency is low. Heat treatment is required to achieve full efficiency. This heat treatment occurs during lamination of the cells in plastic, where the cell is heated under pressure to a temperature of about 225°C for about 15 minutes. The cells used in this study were rectangular with a total area of 2 square centimeters.

Measurement of Spectral Response in the Presence of Bias Light

High intensity grating monochromators with about a 200 \AA ($2 \times 10^{-6}\text{ cm}$) bandwidth were used for the spectral response measurements. The entire cell was illuminated with light from two monochromators: one providing variable wavelength light (hereafter called primary light); the other providing constant intensity, constant wavelength secondary light (hereafter called bias light). The cell was loaded near short circuit current with a 10-ohm resistor and the photocurrent through the resistor was measured with a microvoltmeter. When bias light was used, the photocurrent resulting from the bias light was nulled out electronically with the zero adjustment of the microvoltmeter. By this procedure, the current indicated by the meter presumably represented only the current produced by the action of the variable wavelength (primary) light. These data were converted to relative quantum yields by dividing the adjusted meter current by the incident radiation flux of variable wavelength light in units of quanta per second. All the spectral response data presented in this report are in terms of the relative quantum yield as defined here.

SPECTRAL RESPONSE OF CADMIUM SULFIDE CELLS WITH STANDARD HEAT TREATMENT

Results

No bias light effects. - The spectral response of CdS cells is bewildering in the variety of effects that can be observed. For measurements in monochromatic light alone (no bias light), the past history of illumination of the cell influences the response.

As shown in figure 2, a dependence of the spectral response on past history is observed when the spectral direction of the measurement is changed. Thus, the response when the wavelength is being increased is different from when the wavelength is being decreased. This effect presumably results from the persistence of photoconductivity. Green or blue light ($0.5 \mu\text{m}$) reduces the series resistance of the cell by its effect on the photoconductive layer in the junction region (ref. 4). (Ref. 4 refers to $0.5 \mu\text{m}$ light as green; however, we choose to call it blue in this report.) This reduction persists up to

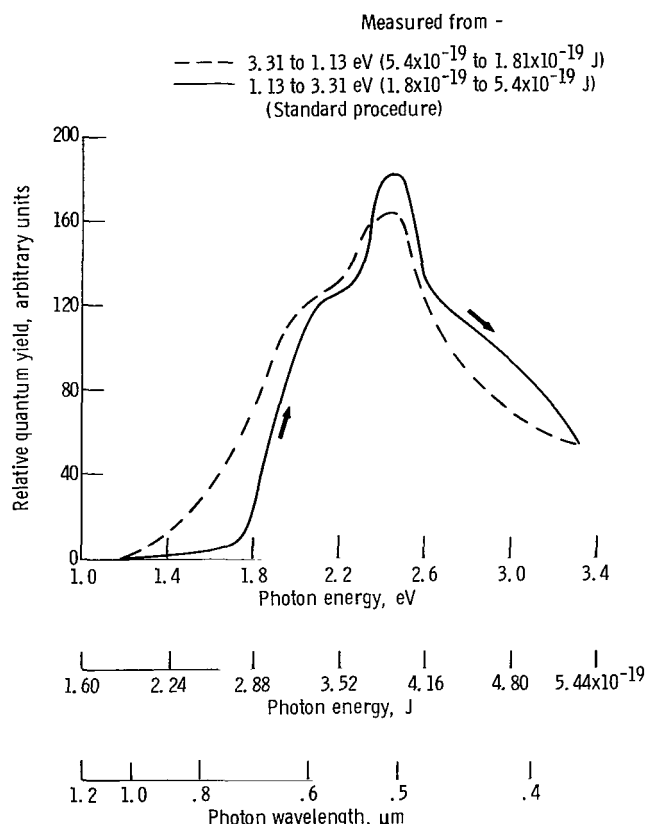


Figure 2. - Spectral response of a CdS solar cell.

tens of minutes after the light is removed. Thus, the red response of the cell is found to be much larger if the measurements are begun in the blue than if they are begun in the red. In the work reported here the response was measured by starting from the red end of the spectrum.

Bias light effects. - When bias light is used, the spectral response depends strongly on the wavelength of the bias light. There is also an effect of the intensity of both the bias and the primary illumination on the spectral response. However, these effects of bias light on the spectral response of the CdS cell appear only after heat treatment of the device. To show this, the spectral response of a diode was measured before heat treatment and no effect of bias light was noted. After a standard heat treatment of 15 minutes at 225°C and without a bias light, practically all of the red response of the cell beyond

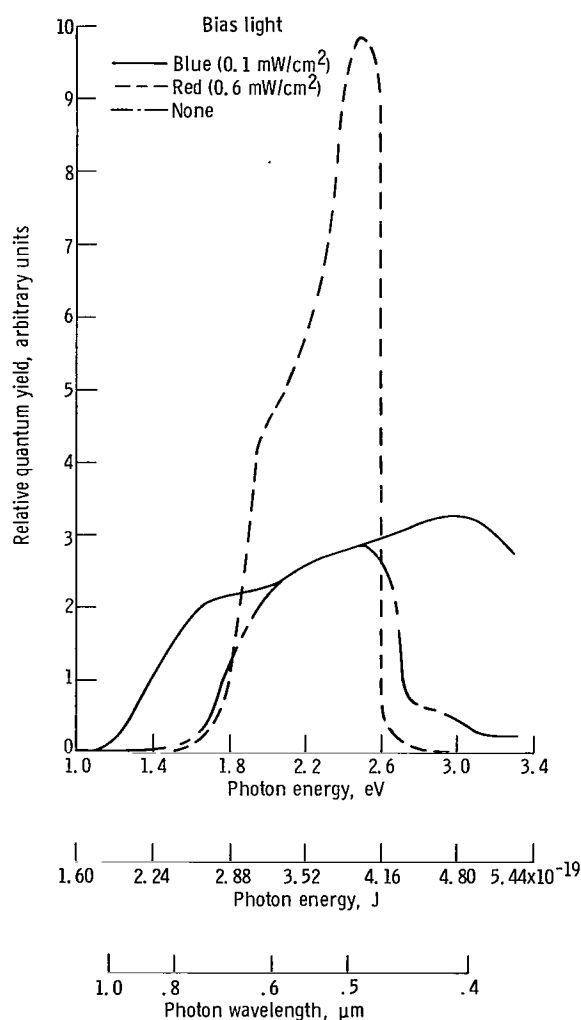


Figure 3. - Spectral response of $\text{Cu}_2\text{S-CdS}$ cell under various bias light conditions.

1.8 eV (2.88×10^{-19} J) was lost. The application of blue bias light essentially restored the quantum yield to its initial value. This effect has been attributed to the formation of a photoconductive layer of copper-doped CdS on heat treatment (ref. 4).

An additional effect occurs under red bias light. Data for a thin film cell under red, blue, and no bias light are shown in figure 3. With no bias light, the curve falls off sharply at 1.8 and 2.7 eV (2.88 to 4.32×10^{-19} J). The falloff in the high energy end is variable from cell to cell. With blue bias light ($0.5 \mu\text{m}$, 2.48 eV; 3.97×10^{-19} J) the response is much broader, falling off at about 1.4 eV (2.24×10^{-19} J) on the low energy side and above 3.3 eV (5.28×10^{-19} J) on the high energy side. When red bias light ($0.9 \mu\text{m}$, 1.37 eV; 2.19×10^{-19} J) is used, however, the relative quantum yield (RQY) falls off sharply at 1.8 and 2.6 eV (2.88 and 4.16×10^{-19} J) similar to the no bias case, but the peak value of the RQY is about a factor of 4 greater than in the previous cases. Depending on the intensity of the red bias light, peak values up to 20 times the RQY in blue light have been obtained. This anomalous increase in RQY will be explained in the Discussion section.

Intensity effects. - The effects of intensity on spectral response were studied by measuring the RQY as a function of bias light intensity. Figure 4 shows the RQY at 0.5 micrometer (blue) as a function of 0.9 micrometer (red) bias light intensity. To make these measurements, the 0.9 micrometer bias light was turned on first and then the primary wavelength region of 1.2 to 0.5 micrometer was swept through. The reading at 0.5 micrometer was then recorded. This procedure was repeated for each intensity of 0.9 micrometer bias light reported. The RQY increases almost linearly with bias light intensity. Two curves are shown, one for a primary light ($0.5 \mu\text{m}$) intensity

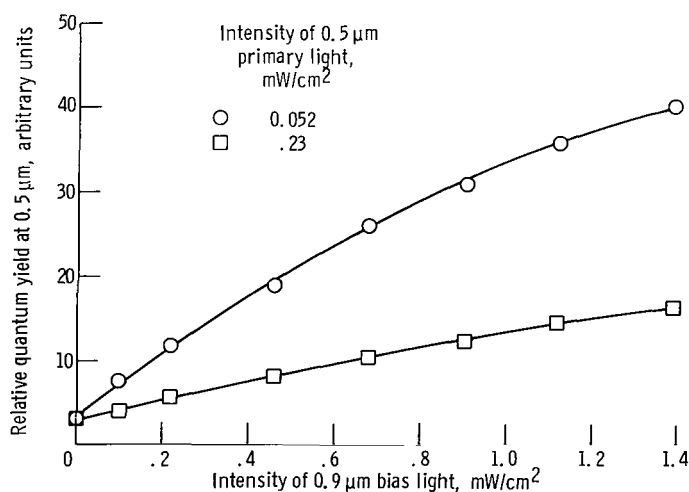


Figure 4. - Effect of increasing red ($0.9 \mu\text{m}$) bias light intensity at constant blue ($0.5 \mu\text{m}$) light intensity.

of 0.052 milliwatt per square centimeter, the other for a primary light intensity of 0.23 milliwatt per square centimeter.

The effect of 0.5 micrometer (blue) bias light intensity on the RQY for two different (0.18 and 1.38 mW/cm²) constant intensities of 0.9 micrometer primary light is shown in figure 5. In contrast to the effect of red bias light, the RQY for blue bias light is seen to saturate above a certain bias light intensity.

Both figures 4 and 5 show that the intensity of the primary light also affects the RQY: the higher the primary light intensity, the lower the RQY.

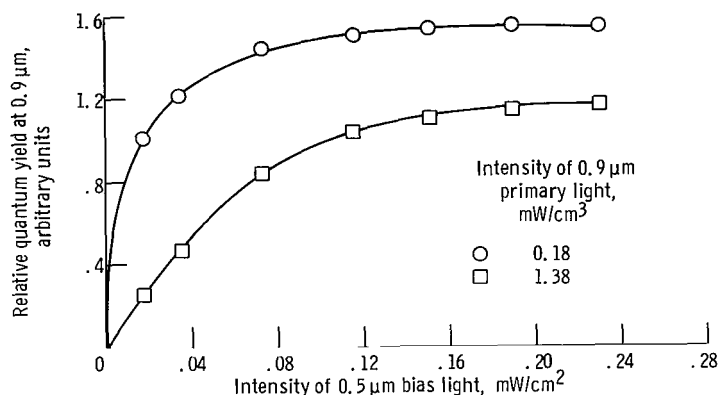


Figure 5. - Effect of increasing blue (0.5 μm) bias light intensity at constant red (0.9 μm) light intensity.

Analysis

A model for the spectral response. - To explain the effects of bias light and light intensity on the spectral response of Cu₂S-CdS cells, the following model is proposed. It is proposed that the cell contains a photoconductive layer which increases in conductivity when illuminated with wavelengths of light between certain energy (gate) values. When illuminated with light of energy values outside these gate values, it remains resistive. This layer reduces the externally observed current by trapping and recombination processes which are negligible when this layer is conductive.

The observed spectral response of the CdS cell under any wavelength, intensity, or combination of bias illuminations is therefore the normal cell response due to photon absorption as modified by the energy gate (and loss) characteristics of the photoconductive layer.

The model incorporating these features is shown schematically in figure 6. If the bias light energy (E_B) lies outside the gate energies (i. e. , $1.8 > E_B > 2.7$ eV, $2.88 > E_B > 4.32 \times 10^{-19}$ J, where 1.8 and 2.7 eV are the low- and high-energy limits of

the gate) the response will be only that of the photoconductive layer. Outside the limits of this layer, the losses will greatly reduce the output.

When the energy of the bias light lies within the gate region (e.g., $1.8 < E_B < 2.7$ eV, $2.88 < E_B < 4.32 \times 10^{-19}$ J), the response due to normal photon absorption results. This occurs because the photoconductive layer is saturated (provided the intensity of the bias light is sufficiently high) and the losses drop to nearly zero.

For the purposes of this model, red bias light and no bias light are expected to be exactly the same and are so noted in figure 6. It should be noted that this is in contra-

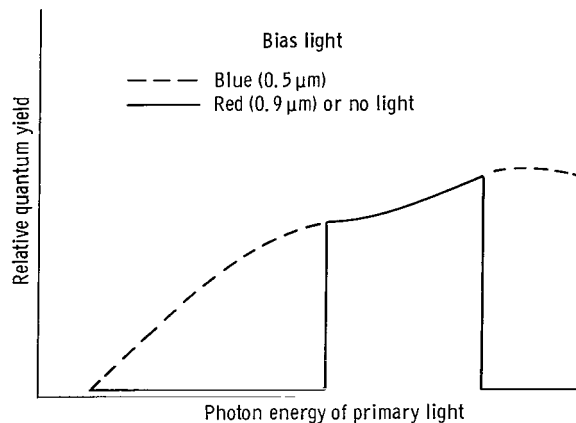


Figure 6. - Model for effect of bias light on spectral response of CdS photovoltaic cells.

diction to the experimental results which indicate a significant difference between red bias light and no bias light conditions (fig. 3). This apparent discrepancy between the model and experimental results will be resolved in the Discussion section.

It should also be noted that the falloff in the blue end is variable from cell to cell. This may indicate that a different mechanism such as interface or surface states is effective in this region. This, however, does not affect the basic model.

Estimation of relative quantum yield. - It is obvious that quantitative predictions of the RQY, based on the proposed model, cannot be made without knowledge of the functional relation between the losses due to the photoconductive layer and the intensity and wavelength of the incident light. This information is not available. Nevertheless, for purposes of analysis and presentation of the complex experimental results, it is of value to develop equations expressing RQY as a function of the light generated current and the current loss terms. Further, it is of use to assume functional forms for the loss terms in order to check the spectral response model against the variety of conditions for which data are available. Nothing concerning the physical mechanism should be inferred from the specific form of the functions chosen.

At this point it would be well to recall that the quantum yield in the presence of bias light is defined as being the total (primary plus bias) photocurrent less the bias light photocurrent (i. e. , the net current), divided by the photon flux from the monochromatic light source:

$$RQY = \frac{I_{net}/e}{AJ/h\nu} \quad (1)$$

and

$$I_{net} = I_{m, p+b} - I_{m, b} \quad (2)$$

where RQY is the relative quantum yield, $I_{m, p+b}$ is the measured short circuit current due to both the primary and the bias light, $I_{m, b}$ is the measured short circuit current due to the bias light alone, e is the electronic charge, A is illuminated cell area, J is the intensity of the primary light, h is Planck's constant, and ν is the frequency of the primary light.

The measured current, however, is subjected to losses due to the photoconductive layer. These losses are possibly caused by trapping the subsequent recombination of the charge carriers. Therefore, the measured current due to the primary plus the bias light can be written as follows:

$$I_{m, p+b} = I_{G, p} + I_{G, b} - I_{L, p+b} \quad (3)$$

where $I_{G, p}$ is the light generated current from the primary light, $I_{G, b}$ is the light generated current from the bias light, and $I_{L, p+b}$ is a loss term due to the photoconductive layer and associated with the presence of both primary and bias light. Similarly,

$$I_{m, b} = I_{G, b} - I_{L, b} \quad (4)$$

where $I_{L, b}$ is a loss term associated with the bias light alone. Substitution into equation (2) yields

$$I_{net} = I_{G, p} - (I_{L, p+b} - I_{L, b}) \quad (5)$$

It is the term in parentheses which will be affected by the various bias conditions.

Substitution of equation (5) into (1) yields the following relation:

$$\mathcal{J}(\text{RQY}) = I_{G, p} - I_{L, p+b} + I_{L, b} \quad (6)$$

where $\mathcal{J} = eAJ/h\nu$. The loss terms $I_{L, p+b}$ and $I_{L, b}$ have values which depend on the wavelengths and intensities of the various illumination conditions.

The relations describing $I_{L, p+b}$ and $I_{L, b}$ in terms of wavelength and intensity of the illumination are chosen as follows:

$$I_{L, p+b} = ce^{\pm aJ_p} \times ce^{\pm bJ_b}$$

$$I_{L, b} = ce^{\pm bJ_b}$$

where a , b , and c are arbitrary constants and J_p and J_b represent the intensities of primary and bias light, respectively; the signs of the exponential are negative when the light is within the photoconductive gate and positive when outside the gate. The proposed relations for the loss terms follow the trend suggested in the model; namely, as the intensity of in-gate light increases, the loss terms decrease, and as the intensity of out-of-gate light increases, the loss terms increase.

Substitution of the loss relations into equation (6) yields the following:

$$\mathcal{J}(\text{RQY}) = I_{G, p} - ce^{\pm bJ_b} \left(ce^{\pm aJ_p} - 1 \right) \quad (7)$$

It should be stressed again that the functional relations for the loss terms were arbitrarily chosen to approximate trends indicated in the model and are not meant to be necessarily descriptive of actual processes.

From the model (fig. 6) it is seen that for red or no bias light when the primary light energy lies outside the gate $\text{RQY} \approx 0$. In other words, under these conditions the sum of the loss terms is approximately equal to the light generated current. The model also assumes that, when the energy of the bias light lies within the gate and is of an intensity great enough to saturate the photoconductive layer, the loss term will drop to zero, that is, $ce^{-bJ_b} = 0$.

From equation (7), equations describing the various effects of illumination wavelength and intensity are derived in the remainder of this section. For convenience, the derivations will be grouped according to type of bias light used.

Red bias light conditions:

$$\mathcal{J}(\text{RQY}) = I_{G,p} - ce^{bJ_b} \left(ce^{\pm aJ_p} - 1 \right) \quad (8)$$

Case A - Energy of primary light lies outside the photoconductive gate: In this instance the loss terms are essentially equal to $I_{G,p}$ and

$$\mathcal{J}(\text{RQY}) = 0 \quad (9)$$

Case B - Energy of primary light lies within the photoconductive gate:

Subcase 1 - Primary light intensity is sufficient to saturate the photoconductive layer, that is, $ce^{-aJ_p} = 0$:

$$\mathcal{J}(\text{RQY}) = I_{G,p} + ce^{bJ_b} \quad (10)$$

Subcase 2 - Primary light intensity is not sufficient to saturate photoconductive layer:

$$\mathcal{J}(\text{RQY}) = I_{G,p} - ce^{bJ_b} \left(ce^{-aJ_p} - 1 \right) \quad (11)$$

Blue bias light conditions:

$$\mathcal{J}(\text{RQY}) = I_{G,p} - ce^{-bJ_b} \left(ce^{\pm aJ_p} - 1 \right) \quad (12)$$

Case A - Bias light intensity sufficient to saturate the photoconductive layer, that is, $ce^{-bJ_b} = 0$:

$$\mathcal{J}(\text{RQY}) = I_{G,p} \quad (13)$$

Case B - Bias light intensity not sufficient to saturate the photoconductive layer:

$$\mathcal{J}(\text{RQY}) = I_{G,p} - ce^{-bJ_b} \left(ce^{\pm aJ_p} - 1 \right) \quad (12)$$

No bias light conditions:

$$\mathcal{J}(\text{RQY}) = I_{G,p} - ce^{\pm aJ_p} \quad (14)$$

Case A - Primary light outside the photoconductive gate:

$$\mathcal{J}(\text{RQY}) = 0 \quad (9)$$

Case B - Primary light inside photoconductive gate:

Subcase 1 - Primary light intensity sufficient to saturate photoconductive layer:

$$\mathcal{J}(\text{RQY}) = I_{G, p} \quad (13)$$

Subcase 2 - Primary light not sufficient to saturate photoconductive layer:

$$\mathcal{J}(\text{RQY}) = I_{G, p} - ce^{-aJ_p} \quad (15)$$

Discussion

Red bias light conditions. - When the primary light sweeps through the spectral region outside the 1.8 to 2.6 eV (2.88 to 4.16×10^{-19} J) energy gate, the measured current will be effectively zero, as shown by equation (9) and figure 3. On the other hand, when the primary light sweeps through the gate region, a current flows because the photoconductive layer becomes less resistive. In addition to the current contribution of the primary light, there will also be a current contribution from the red bias light. This is indicated by equation (10), which shows that the net current measured is greater than the light generated current by an amount equal to the bias light loss term. The contribution of the red bias light loss term is an artifact of the measurement technique: the nulling technique assumes a constant bias light contribution throughout the spectral region measured and does not allow for a photoconductive effect.

Because of the erroneously large values of RQY obtained (see fig. 3), it is evident that the relative quantum yield in the presence of red bias light can have little meaning except as a qualitative measure of the response spectrum of the photoconductive layer in the cell. For the limiting case where the red bias light intensity is very much larger than the primary light intensity, the photocurrent from the cell is primarily from the red light and is limited by the resistance of the photoconductive layer. As primary light changes the resistance of this layer, the current from the red light changes accordingly. The primary light, therefore, is acting much as the electrical bias in an electron tube amplifier. It follows that, to a first approximation, the response of the cell with high-intensity red bias light represents the excitation spectrum of the photoconductive layer in the cell. The red bias light curve in figure 3 was measured under high bias light in-

tensity and therefore should show the response of the photoconductive layer. There is a primary peak near 2.5 eV (4.00×10^{-19} J), close to the band edge of CdS (2.4 eV, 3.84×10^{-19} J). A secondary peak appears at about 2.0 eV (3.20×10^{-19} J) and little response occurs in the infrared region beyond 1.8 eV (2.88×10^{-19} J). This response is typical of copper-doped CdS layers (ref. 6).

From figure 4, it can be seen that when the primary light wavelength is held constant at 0.5 micrometer, the RQY increases approximately linearly with the red (0.9 μ m) bias light intensity. This is to be expected from equation (10) because the exponential term is approximately linear at low intensities. The curve does appear to bend over toward some saturated value, which is reasonable. No attempt was made to include the effects of saturation for the red bias light case in this simple model nor in the arbitrary functional relations for the loss terms.

If the intensity of primary light is not sufficient to saturate (first case B, sub-case 2), equation (11) results. In this case, too, it is expected that when the primary light wavelength is held constant at 0.5 micrometer, the RQY will increase linearly with red bias light intensity. The data plot of figure 4 for blue primary light of 0.052 milliwatt per square centimeter agrees with this relation at low red bias light intensities.

Although the curves of figure 4 do approximate the predicted straight lines from equations (10) and (11), the difference in slope between the two curves is opposite to that predicted from equations (10) and (11). The difference in slope between the two curves may result from the high series resistance in the cells tested. The limiting effect of series resistance on cell current, and hence the relative quantum yield, becomes more important as the current is made larger by increased light intensity. Consequently, a lower quantum yield would be observed at a higher primary light intensity.

It is believed that the differences in RQY shown in figure 4 under the different intensities of both primary and bias illumination account for the variety of spectral response curves customarily obtained for CdS cells. The results presented here indicate that when spectral responses for CdS cells are reported it is necessary to specify both the primary and the bias light intensity. Otherwise, comparisons of test data may not be meaningful.

Blue bias light conditions. - Equations (12) and (13) describe the results when the bias light lies within the photoconductive gate and the intensity is not and is, respectively, sufficient to saturate the photoconductive layer. Under high blue light intensities, the response is indicative of the normal photon absorption in the cell (see fig. 3). The blue bias light lowers the cell resistance to a minimum value (presumably by filling copper centers). Once this has been done, it does not matter if other wavelengths are added to the blue light. Consequently, white bias light might be used, but in order to get

reproducible results, the intensity of blue light contained in the white must be high enough to saturate the photoconductive layer in the cell.

The effect of blue ($0.5 \mu\text{m}$) bias light intensity on the RQY is shown in figure 5. The curves approximate the relation shown by equation (12) and indicate that saturation of the copper centers (eq. (13)) takes place at a blue light intensity of about 0.23 milliwatt per square centimeter. When the red light intensity is made greater, the term $\left(\frac{aJ}{ce^p} - 1\right)$ of equation (12) increases and therefore saturation of the RQY should occur at a higher intensity of blue bias light, as indicated by the lower curve of figure 5.

It should be noted that the RQY in figures 4 and 5 does not cross-check. For example, in figure 4, with a 0.9-micrometer bias light intensity of 1.38 milliwatts per square centimeter and a primary light intensity of 0.23 milliwatt per square centimeter (wavelength constant at $0.5 \mu\text{m}$), the RQY is 16.8. In figure 5, with the 0.5 micrometer light treated as the bias light, the RQY for the same intensities is 1.16. The higher value of the RQY in figure 4 is another illustration of the spurious increase in RQY with red bias light due to the technique of measurement.

No bias light conditions. - If no bias light is present, there will be a loss in current when the energy of the primary light is outside the photoconductive gate. The loss term is essentially equal to $I_{G,p}$; hence the output drops essentially to zero, as indicated by equation (9).

When the primary light lies within the gate and the intensity is sufficient to saturate the photoconductive layer (case B, subcase 1, eq. (13)), the loss term vanishes and the response is indicative of the normal photon absorption in the cell, as shown in figure 3. This case is identical to the high-intensity blue bias light case. If the primary light intensity is not sufficient to saturate, a loss term will be present, as shown in equation (15). Under this condition, lower values of the RQY intermediate between the two extremes will be obtained.

SPECTRAL RESPONSE OF A CADMIUM SULFIDE CELL AS A FUNCTION OF HEAT TREATMENT

Heat treatment is an important step in the fabrication of efficient cells. Before heat treatment the junction characteristic of the cell is poor, as indicated by a large reverse saturation current. Heat treatment improves the characteristic but decreases the short circuit current. It has also been observed that the spectral response is dependent on heat treatment. The effect of bias light on spectral response does not appear until after heat treatment. This has been explained (ref. 4) as due to diffusion of copper into the junction to form a photoconductive layer of copper-compensated cadmium sulfide.

A finished cell receives a heat treatment of about 15 minutes at 220° to 230° C as a result of lamination. The rate at which this heat treatment produces changes in the spectral response was studied by heating a cell for various intervals of time. The cell was given five heat treatments at a constant temperature of 220° C. The first heat treatment was for 1/2 minute, the next two were each for 3 minutes, and the last two were for 5 minutes. The changes in the RQY, reported for totaled heating times, are shown in figure 7(a) without bias light and in figure 7(b) with 0.5-micrometer (blue) bias

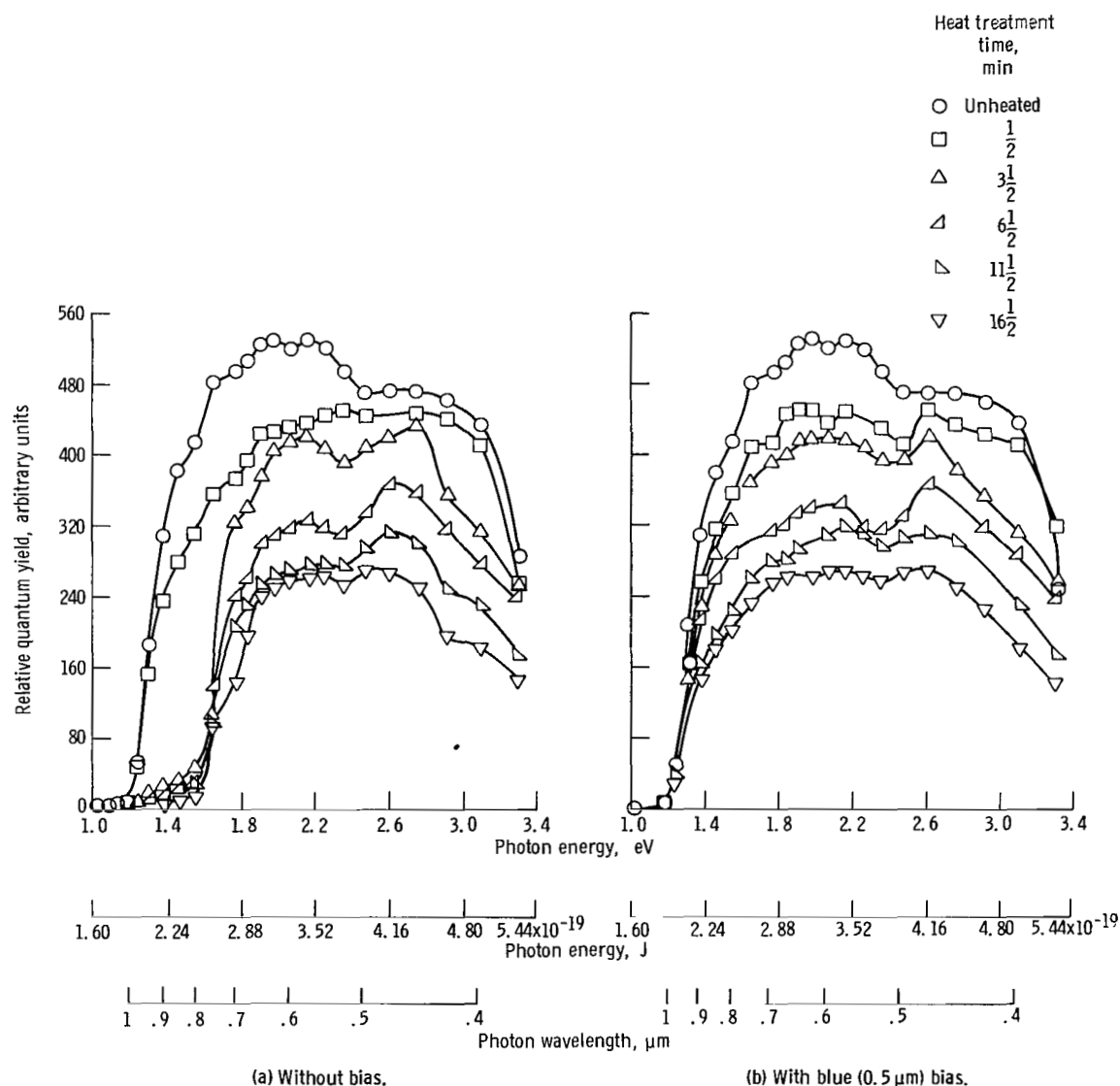


Figure 7. - Effect of heat treatment time at 220° C on the spectral response of a CdS cell.

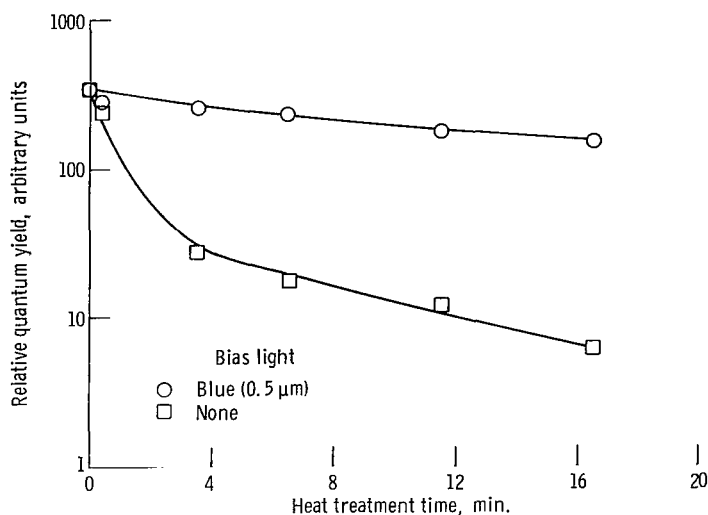


Figure 8. - Effect of heat treatment time at 220° C on the response of a CdS cell to 1.4 eV (2.24×10^{-19} J; 0.885 μ m) light.

light. The units are arbitrary and cannot be compared to those of figures 3 to 5 (although figs. 8 and 9 are comparable).

The first heat treatment of $1/2$ minute produced only slight variations between the unbiased and 0.5-micrometer biased curves with both showing a small loss in RQY. Additional heatings totaling $16\frac{1}{2}$ minutes showed a continued decrease in response with pronounced drops in the unbiased spectral response curves in the red wavelength region (1.0 to 1.8 eV; 1.60 to 2.88×10^{-19} J). Most of this drop occurred between the first two heat treatments, as shown in figure 8, where the RQY for a wavelength of 0.885 micrometer (1.4 eV; 2.24×10^{-19} J) is plotted against the total heating times. Between $1/2$ and $3\frac{1}{2}$ minutes of heating, the unbiased curve showed a drop in response from approximately 250 to 27 (factor of about 9), while with a 0.5-micrometer bias light, the change was small. The overall drop for $16\frac{1}{2}$ minutes of heating was a factor of 55 without bias light and only a factor of about 2 with 0.5-micrometer bias light.

Thus, the onset of the decay in the red wavelength response without bias light occurred in the first several minutes of heating and then progressed somewhat more slowly. This loss in red response is largely nullified if 0.5-micrometer bias light is used. Even with blue bias light, however, a significant loss of overall response occurs. The heat treatment is thus seen to be undesirable from the point of view of quantum yields. If the heat treatment required to produce a junction with good electrical characteristics could be eliminated or shortened, a gain in conversion efficiency might result.

The effect of heat treatment on the response with red (0.9 μ m) bias light is shown in figure 9. The curve obtained at $11\frac{1}{2}$ minutes of heating has been deleted for clarity. As previously mentioned, the response with red bias light has no meaning in terms of

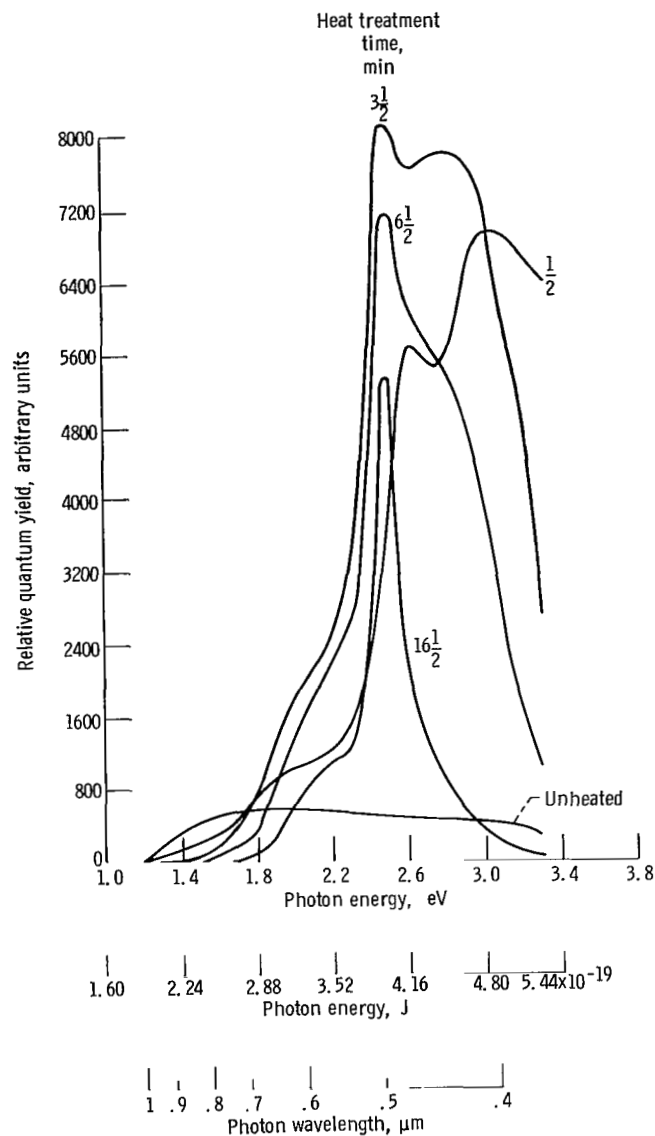


Figure 9. - Effect of heat treatment time at 220° C on the spectral response of a CdS cell. Measured with red (0.9 μm) bias light.

relative quantum yield, but should be viewed as an approximate representation of the excitation spectrum of the photoconductive layer in the cell. The data shown in figure 9 display a gradual shift in this spectrum with heat treatment. After a very short heat treatment (1/2 min), the response is peaked near 3.0 eV (4.80×10^{-19} J), and is quite broad, extending from 1.8 eV (2.88×10^{-19} J) to beyond 3.4 eV (5.44×10^{-19} J). At $3\frac{1}{2}$ minutes the total response has reached a maximum, and a strong peak at 2.5 eV (4.00×10^{-19} J) is developed. The broad peak around 3.0 eV (4.80×10^{-19} J) of the 1/2-minute heat treatment has decreased. As the heat treatment continues, the overall response drops, as does the broad peak around 3.0 eV (4.80×10^{-19} J), until at $16\frac{1}{2}$ minutes only the peak at 2.5 eV (4.00×10^{-19} J) remains.

This behavior is consistent with the idea that the photoconductive layer is formed by diffusion of copper into the cadmium sulfide. The first copper to diffuse into the CdS (1/2 min of heating) forms a narrow photoconductive layer near the surface and the 3.0-eV (4.80×10^{-19} J) light interacts with this layer. At longer diffusion times, the copper goes deeper into the CdS. In this instance, the high energy photons are mostly absorbed before they reach the deeper copper centers. Thus there is little effect on the photoconductive layer and hence the falloff shown in figure 9 occurs. For these conditions only band gap illumination (2.5 eV; 4.00×10^{-19} J) can be effective. Also supporting the connection between the photoconductive layer and diffused copper is the slight response near 2.0 eV (3.20×10^{-19} J), which corresponds to the reported photoconductivity excitation spectrum of copper in CdS (ref. 6).

CONCLUSIONS

The dependence of the spectral response of cadmium sulfide cells on the wavelength and intensity of bias light can be satisfactorily interpreted in terms of a blue-sensitive photoconductive layer in the junction region of the cell. This layer is formed in the junction region by diffusion of copper into the cadmium sulfide during heat treatment.

Measurements in the absence of bias light are ambiguous because past illumination history of the cell influences the results. Therefore, in order to obtain spectral response curves that are reproducible and indicative of the absorption spectrum of the cell when it is operating as a photovoltaic device in sunlight, blue (0.5- μ m) bias light with an intensity high enough to saturate the copper centers must be used. On the other hand, if a measurement of the spectral response (excitation spectrum) of the photoconductive layer is desired, the measurement can be made under red bias light; the values of the relative quantum yield so obtained will be erroneously high as a consequence of the measurement technique. Additionally, to allow for a meaningful comparison of results, it is necessary to specify the intensity of both the primary and the bias light.

Although heat treatment is necessary to improve the junction characteristics, it considerably reduces the quantum yield of the cell. Presumably, if the heat treatment required to produce good electrical characteristics were eliminated or shortened, a gain in conversion efficiency might result.

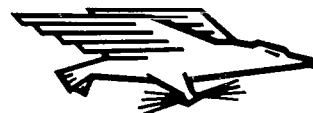
Lewis Research Center,
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